

# PATENT SPECIFICATION

(11)

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- (21) Application No. 46891/72 (22) Filed 11 Oct. 1972  
 (31) Convention Application No.  
 188 605 (32) Filed 12 Oct. 1971 in  
 (33) United States of America (US)  
 (44) Complete Specification published 6 Aug. 1975  
 (51) INT. CL. G03G 9/00 // 9/14  
 (52) Index at acceptance

G2H 12 1J4 1JY 1Y 2B 2X 2Y 5A 5D1A 5D1Y 5DY 5Y



## (54) ELECTROSTATOGRAPHIC DEVELOPING MATERIAL

(71) We, XEROX CORPORATION of Xerox Square, Rochester, New York 14603, United States of America, a body corporate organized under the laws of the 5 State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an electrostatographic developing material and its use in developing an electrostatic latent 15 image comprised by a surface.

The formation and development of images on the surface of photoconductive materials by electrostatic means is well known. The basic electrophotographic 20 process, as taught by C. F. Carlson in U.S. Patent 2,297,691, involves placing a uniform electrostatic charge on a photoconductive insulating layer, exposing the layer to a light and shadow image to dissipate the charge on the areas of the layers exposed to the light and developing the resulting electrostatic latent image by depositing on the image a finely divided electroscopic material referred to in the art as 25 "toner". The toner will normally be attracted to those areas of the layer which retain a charge thereby forming a toner image corresponding to the electrostatic latent image. This powder image may then 30 be transferred to a support surface such as paper. The transferred image may substantially be permanently affixed to the support surface as by heat. Instead of latent image formation by uniformly charging the photoconductive layer and then exposing the layer to a light and shadow image, one may form the latent image by 35 directly charging the layer in image configuration. The powder image may be fixed 40 to the photoconductive layer if the powder

image transfer step is not desired. Other suitable fixing means such as solvent or overcoating treatment may be substituted for the foregoing heat fixing step.

Several methods are known for applying the electroscopic particles to the electrostatic latent image to be developed. One development method, as disclosed by E. N. WISE in U.S. Patent 2,618,552, is known as "cascade" development. In this method, 50 a developer material comprising relatively large carrier particles having finely divided toner particles electrostatically coated thereon is conveyed to and rolled or cascaded across the electrostatic image bearing surface. The composition of the carrier particles is so selected as to triboelectrically charge the toner particles to their desired polarity. As the mixture cascades or rolls across the latent image bearing surface, the toner particles are electrostatically deposited and secured in positive development processes to the charged portion of the latent image and are not deposited on the uncharged or 55 background portions of the image. Most of the toner particles accidentally deposited in the background areas are removed by the rolling carrier, due apparently, to the greater electrostatic attraction between the toner and the carrier than between the toner and the discharged background. The carrier and excess toner are then recycled. 60 This technique is extremely good for development of line copy images. 65

Another method for developing electrostatic images is the "magnetic brush" process as disclosed, for example, in U.S. Patent 2,874,063. In this method, a developer material containing toner particles 85 and magnetically attractive carrier particles are carried by a magnet. The magnetic field of the magnet causes alignment of the magnetically attractive carrier particles into a brushlike configuration. This 90

"magnetic brush" is engaged with the electrostatic image bearing surface and the toner particles are drawn from the brush to the latent image by electrostatic attraction.

Still another technique for developing electrostatic latent images is the "powder cloud" process as disclosed, for example, by C. F. Carlson in U.S. Patent 2,221,776.

- 10 In this method, a developer material comprising electrically charged toner particles in a gaseous fluid is passed adjacent the surface bearing the electrostatic latent image. The toner particles are drawn by 15 electrostatic attraction from the gas to the latent image. This process is particularly useful in continuous tone development.

Other development methods such as "touchdown" development as disclosed by 20 R. W. Gundlach in U.S. Patent 3,166,432 may be used where suitable.

- Generally, commercial electrostatographic development systems utilize automatic machines. Since automatic electrostatographic imaging machines should operate with a minimum of maintenance, the developer employed in the machines should be capable of being recycled through many thousands of cycles. In 30 automatic xerographic equipment, it is conventional to employ an electrophotographic plate which is charged, exposed and then developed by contact with a developer mixture. In some automatic machines, the toner image formed on the electrophotographic plate is transferred to a receiving surface and the electrophotographic plate is then cleaned for reuse. Transfer is effected by a corona generating device 35 which imparts an electrostatic charge to attract the powder from the electrophotographic plate to the recording surface. The polarity of charge required to effect image transfer is dependent upon the visual form of the original copy relative to 40 the reproduction and to the electroscopic characteristics of the developing material employed to effect development. For example, where a positive reproduction is to 45 be made of the positive original, it is conventional to employ a positive corona to effect transfer of a negatively charged toner image to the recording surface. When a positive reproduction from a negative original is desired, it is conventional to 50 employ positively charged toner which is repelled by the charged areas on the plate to the discharged areas thereon to form a positive image which may be transferred by 55 negative polarity corona. In either case, a residual powder image usually remains on the image after transfer. Because the plate may be reused for a subsequent cycle, it is necessary that the residual image be removed to prevent "ghost images" from for-

ming on subsequent copies and toner film from forming on the photoreceptor surface. In a positive to positive reproduction process described above, the residual powder is tightly retained on the plate surface 70 by a phenomenon not fully understood which prevents complete transfer of the powder to the support surface, particularly in the image area. Incomplete transfer of toner particles is undesirable because 75 image density of the ultimate copy is reduced and highly abrasive photoreceptor cleaning techniques are required to remove the residual toner from the photoreceptor surface. This imaging process is ordinarily 80 repeated for each copy reproduced by the machine any time during the reusable life of the developer and the electrostatographic plate surface.

Various electrostatographic plate cleaning devices such as the "brush" and the "web" cleaning apparatus are known in the prior art. A typical brush cleaning apparatus is disclosed by L. E. Walkup et al in U.S. Patent 2,832,977. The brush type 85 cleaning means usually comprises one or more rotating brushes, which remove residual powder from the plate into a stream of air which is exhausted through a filtering system. A typical web cleaning device 90 is disclosed by W. E. Graff, Jr. et al in U.S. Patent 3,186,838. As disclosed by Graff, Jr. et al, removal of the residual powder on the plate is effected by passing a web of fibrous materials over the plate surface. 100 Another system for removing residual toner particles from the surface of a photoreceptor comprises a flexible cleaning blade which wipes or scrapes the residual toner from the photoreceptor surface as the surface moves past the blade. 105

Unfortunately, the foregoing cleaning systems do not effectively remove all types of toner particles from all types of reusable photoreceptors. This is not a shortcoming 110 of the cleaning system, but a shortcoming of particular toners used in conjunction with particular photoreceptors. If a particular toner would not tend to form an adherent residual film on a particular 115 photoreceptor, the cleaning systems described would effectively remove all residual toner. However, many commercial toners of their very nature do tend to form a residual film on reusable photoreceptors. 120 The formation of such films is undesirable because it adversely affects the quality of undeveloped and developed images. The toner film problem of these particular toners is acute in high speed copying and 125 duplicating machines where contact between the developer and the imaging surface occurs a great many more times and at a higher velocity than in conventional electrostatographic systems. Ultimately, the 130

toner buildup becomes so great that effective copying or duplicating is impaired. As a result, more stringent means, e.g. solvent removal, are necessary to remove this type 5 of film. Frequent shutdown of the apparatus, in order to clean the surface of the photoreceptor is obviously undesirable since the machine is taken out of commission and repeated techniques of this type 10 wear down the photoreceptor surface.

Thus, there is a continuing need for a technique for eliminating the buildup of toner film on the surface of a photoreceptor. Electrostatographic systems and, 15 in particular, the imaging, developing and cleaning aspects of such systems would be significantly advanced if the foregoing problems were effectively overcome.

Accordingly, it is an object of the invention to provide a developer composition which effectively eliminates toner film 20 buildup.

It is another object of the invention to provide a developer composition which improves solid area print density.

It is a further object of the invention to provide a developer composition which reduces background density of copies.

It is yet another object of the invention 30 to provide a developer composition having enhanced and stabilized triboelectric characteristics.

It is still another object of the invention to provide a developer composition which 35 permits effective long term prevention or control of toner filming on a reusable photoreceptor.

A still further object of the invention is to provide a developer composition of increased life, i.e., more prints per unit 40 weight of developer.

Still another object of the invention is to provide a developer composition which yields copies of comparatively high optical 45 density.

It is another object of the invention to provide a process which prevents undesirable buildup of developer components on reusable electrostatographic imaging 50 surfaces.

It is a further object of this invention to provide an electrostatographic imaging process employing developing materials which provides for more effective cleaning 55 of reusable electrostatographic imaging surfaces.

It is another object of this invention to provide an electrostatographic imaging process employing developer mixtures 60 which are readily transferable from an electrostatographic surface to a transfer surface.

A further object of the invention is to provide an improved developer composition and process which yields images 65

and copy with no loss of resolution.

Yet a further object is to provide an improved developer composition and process with no loss in fusing efficiency.

A still further object of the invention is to provide an improved developer composition having less tendency for toner blocking.

A further object of the invention is to provide an improved developer composition which increases the life of imaging surface cleaning members.

The present invention provides an electrostatographic developing material in accordance with Claim 1 appended hereto, 80 and a process of developing an electrostatic latent image in accordance with Claim 9 appended hereto. Preferences for this process and the developing material are given in the remaining appended claims. 85

The toner material of the present invention may be any electroscopic toner material which preferably is pigmented or dyed. Typical toner materials include polystyrene resin, acrylic resin, polyethylene 90 resin, polyvinyl chloride resin, polyacrylamide resin, methacrylate resin, polyethylene terephthalate resin, polyamide resin, and copolymers, polyblends and mixtures thereof. Vinyl resins having a melting 95 point or melting range starting at 110°F are especially suitable for use in the toner of this invention. These vinyl resins may be a homopolymer or a copolymer of two or more vinyl monomers. Typical 100 monomeric units which may be employed to form vinyl polymers include: styrene; vinyl naphthalene; mono-olefins, such as, ethylene, propylene, butylene, or isobutylene; vinyl esters, such as vinyl acetate, 105 vinyl propionate, vinyl benzoate, or vinyl butyrate, esters of aliphatic acids such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, dodecyl acrylate, 110 n-octyl acrylate, methyl methacrylate, ethyl methacrylate or butyl methacrylate; vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, or vinyl ethyl ether; vinyl ketones such as vinyl methyl ketone, vinyl 115 hexyl ketone or methyl isopropenyl ketone; and mixtures thereof. Suitable materials employed as the toner will usually have an average molecular weight between 3,000 to 120 500,000.

Any suitable pigment or dye may be employed as the colorant for the toner particles. Toner colorants are well known and include, for example, carbon black, nigrosine dye, aniline blue, Calco Oil Blue, chrome yellow, ultramarine blue, duPont Oil Red, quinoline yellow, methylene blue chloride, phthalocyanine blue, Malachite Green Oxalate, lamp black, Rose Bengal and mixtures thereof. The pigment or dyes 130

should be present in the toner in a sufficient quantity to render it highly coloured so that it will form a clearly visible image on a recording member. Thus, for example, 5 where xerographic copies of typed documents are desired, the toner may comprise a black pigment such as carbon black or a black dye such as Amaplast Black Dye available from the National Aniline 10 Products, Incorporated. Preferably, the pigment is employed in an amount of from 1% to 30%, by weight, based on the total weight of the colored toner. If the toner colorant employed is a dye, substantially 15 smaller quantities of the colorant may be used.

When the toner materials of the present invention are to be employed in the aforementioned development processes, the 20 toner should have an average particle size by weight percent less than 30 microns.

The metal salt of a fatty acid is capable 25 of forming an adherent film deposit on the imaging surface of a reusable photoreceptor during the repeating cycles of an electrostatographic system. This salt need not be one which will form a completely continuous film on the imaging surface, although many will form a continuous film. 30 Other metal salts of fatty acids will tend to fill the valleys of the surface and minute peaks will be coated with no more than a monolayer of the salt. The melting point of the metal salt is limited mainly by the ambient operating conditions and obviously 35 should be at least somewhat higher than the ambient temperature.

The metal salts may be salts of saturated or unsaturated, substituted or unsubstituted fatty acids, preferably of from 40 8 to 35 carbon atoms. The metal salts of the above identified fatty acids include, but are not limited to, the lithium, sodium, potassium, copper, rubidium, silver, magnesium, calcium, zinc, strontium, cadmium, barium, mercury, aluminum, chromium, tin, titanium, zirconium, lead, manganese, iron, cobalt and nickel salts and mixtures of said salts. Specific fatty acids contemplated include caprylic, pelargonic, capric, undecanoic, lauric, tridecanoic, myristic, pentadecanoic, palmitic, margaric, stearic, arachidic, behenic, lignoceric, cerotic and mixtures thereof.

55 When a developer composition containing a metal salt of a fatty acid as the additive is employed for general copying purposes, there is noted an excessive build-up of this additive on the imaging surface 60 in somewhat the same fashion as toner without an additive builds up. This build-up is also particularly acute in high speed copying and duplicating machines where contact between the developer and the imaging surface occurs a great many more

times and at higher velocities than in conventional electrostatographic systems. It was discovered that the utilization of modified silicon dioxide particles as specified in claim 1 appended hereto could be employed in conjunction with the friction-reducing material with outstanding success. 70

With no intention of being bound by any theory of action, it is believed that a metal salt of a fatty acid, if used as the sole developer additive, forms a lubricating film on an imaging surface more easily and to the essential exclusion of a toner film. This film not only permits more effective removal of residual toner material but also 80 increases the life and efficiency of any cleaning member used to remove residual developer. During use, however, the metal salt of a fatty acid will build up to an extent which gradually degrades the quality 85 of copies. By including in the developer composition a minor proportion of modified silicon dioxide particles as specified in claim 1 appended hereto, this material will control the buildup of the metal salt of a 90 fatty acid by its abrasive action when a cleaning means removes residual developer from an imaging surface with a force which causes the developer mixture to be wiped across at least a portion of the imaging surface. This combination of additives permits the metal salt of a fatty acid to perform its function while the abrasive material prevents an excessive, interference layer of lubricant from building 95 up. In addition, the proper triboelectric difference between a charging means, e.g. carrier particles, and the toner material is at least stabilized since the modified silicon dioxide particles specified in claim 1 appended hereto prevent a nullifying buildup 100 of toner on the charging means.

Preferred modified silicon dioxide particles specified in claim 1 appended hereto are prepared by reacting freshly prepared 110 colloidal silica with at least one organosilicon compound having organic groups as well as hydrolyzable groups attached to its silicon atom. In one technique, the reactants and steam are 115 pneumatically introduced in parallel flow into a fluidized bed reactor heated to substantially 400°C. The organosilicon compound reacts with silanol groups on the surface of the SiO<sub>2</sub> particles and chemical 120 attachment between the silicon atom in the organosilicon compound and the silicon atom in the SiO<sub>2</sub> occurs through an oxygen atom. Any suitable organic group directly attached to a silicon atom in the 125 organosilicon compound may be employed in preparing the modified silica. The organic group is preferably one which imparts hydrophobic characteristics to the abrasive material to improve the stability of 130

developer materials under varying humidity conditions. The organic groups may comprise saturated or unsaturated substituted or unsubstituted hydrocarbon groups or derivatives thereof. Saturated organic groups include methyl, ethyl, propyl, butyl, chloropropyl and chloromethyl groups. Examples of typical organosilicon compounds include: dimethyl dichlorosilane, trimethyl 5 chlorosilane, methyl trichlorosilane, vinyl triethoxy silane. The type of organo groups can influence the triboelectric characteristics of the developer. For example, silica treated with aminopropylsilane can 10 be used in a reversal type developer.

The average particle size of the modified silicon dioxide particles additive should preferably fall within the submicron range of from substantially 1 to substantially 500 15 millimicrons and most preferably, between substantially 10 to substantially 100 millimicrons.

There is no particular criticality surrounding the shape of each said modified 20 silicon dioxide particle since both spherical and irregularly shaped particles function effectively. A preferred material is Aerosil R972, a hydrophobic silica available from DeGussa Incorporated, New York, New 25 York. "Aerosil" is a registered trademark.

The composition of the present invention finds utility in all known electrostatographic development systems. This includes systems which employ a carrier 30 material such as magnetic brush development and cascade development as well as systems which do not necessarily employ a carrier material such as powder cloud development, fiber brush development and touchdown development.

Suitable coated and uncoated carrier materials for cascade development are well known in the art. The carrier particles comprise any suitable solid material, provided 45 that the carrier particles acquire a charge having an opposite polarity to that of the toner particles when brought in contact with the toner particles so that the toner particles cling to and surround the carrier 50 particles. When a positive reproduction of the electrostatic images is desired, the carrier particles are selected so that the toner particles acquire a charge having a polarity opposite to that of the electrostatic image. 55 Alternatively, if a reversal reproduction of the electrostatic image is desired, the carrier is selected so that the toner particles acquire a charge having the same polarity as that of the electrostatic image. Thus, 60 the materials for the carrier particles are selected in accordance with its triboelectric properties in respect to the electroscopic toner so that when mixed or brought into mutual contact, one component of the 65 developer is charged positively if the other

component is below the first component in a triboelectric series and negatively if the other component is above the first component in a triboelectric series. By proper selection of materials in accordance with 70 their triboelectric effects, the polarities of their charge, when mixed, are such that the electroscopic toner particles adhere to and are coated on the surface of carrier particles and also adhere to that portion of 75 the electrostatic image bearing surface having a greater attraction for the toner than the carrier particles. Typical carriers include: steel, flintshot, aluminum potassium chloride, Rochelle salt, nickel, potassium 80 chloride, granular zircon, granular silica, methyl methacrylate, or glass. The carriers may be employed with or without a coating. Many of the foregoing and other typical carriers are described in U.S. Patent 85 2,618,552. An ultimate coated particle diameter between 50 microns to 2000 microns is preferred because the carrier particles then possess sufficient density and inertia to avoid adherence to the electrostatic 90 images during the cascade development process. Adherence of carrier beads to electrostatic drums is undesirable because of the formation of deep scratches on the 95 surface during the image transfer and drum cleaning steps. Also, print deletion occurs when large carrier beads adhere to xerographic imaging surfaces. For magnetic brush development, carrier particles having an average particle size less than 800 microns 100 are satisfactory. Generally speaking, satisfactory results are obtained when 1 part toner is used with 10 to 1000 parts by weight of carrier in the cascade and magnetic brush developers.

Concerning the broad relative proportions of the toner material versus the additive materials, functionally stated, the metal salt of a fatty acid should be present in a proportion at least sufficient to form 110 an adherent deposit substantially uniformly distributed over at least 20% of the area of an imaging surface during cyclic use of the imaging surface. It is preferred, that 115 100% of the imaging area becomes coated with the metal salt of a fatty acid. It has been found that from 0.01 to 10% by weight of a metal salt of a fatty acid based on the weight of the toner material will achieve the foregoing degree of coverage. A 120 particularly preferred ratio is from 0.1% to 2.0% by weight of metal salt based on the weight of toner.

Functionally stated, the modified silicon dioxide particles specified in claim 125 1 appended hereto must be present in a relative proportion sufficient to maintain the thickness of the metal salt film deposit within the sub-micron range i.e. less than 10,000Å, in 130

order to avoid having an interference film, yet this proportion must not be so great as to completely remove the deposit or prevent one from forming. If the relative proportion is so great that no film is retained or formed, the modified silicon dioxide particles recited in claim 1 appended hereto will be acting directly on the photoreceptor and for long term operation this can contribute to shortening the life of the photoreceptor and certain of the cleaning means employed in the system. As a lower limit, as long as 5Å of the metal salt is available on the imaging surface the benefits of the present invention will be realized. One skilled in the art can readily determine optimum ratios of the dual additives by monitoring the thickness of the residual friction-reducing film. The use of a radioactive tracer in the metal salt is one effective means of optimizing proportions. Comparative long term runs will also be of assistance. Generally, it has been found that from 0.01% to 10% by weight of modified silicon dioxide particles specified in claim 1 appended hereto based on the weight of the toner material will achieve the desired results. A particularly preferred range is from 0.1 to 2.0% by weight.

30 The developing material of the present invention may be employed to develop electrostatic latent images on any suitable electrostatic latent image bearing surface including photoconductive surfaces. Well known photoconductive materials include: vitreous selenium, organic or inorganic photoconductors embedded in a non-photoconductive matrix, organic or inorganic photoconductors embedded in a 40 photoconductive matrix. Representative patents in which photoconductive materials are disclosed include: U.S. Patent 2,803,542 to Ullrich, U.S. Patent 2,970,906 to Bixby, U.S. Patent 3,121,006 to Middleton, U.S. Patent 3,121,007 to Middleton and U.S. Patent 3,151,982 to Corsin.

In U.S. Patent 2,986,521, Wielicki, there is taught a reversal type developer powder for electrostatic printing comprising electroscopic material, i.e. toner, coated with a finely divided colloidal silica. The toner material must have (1) a positive triboelectric relationship with respect to the silica and (2) the silica coated toner must be repelled from negatively charged areas of an imaging surface. The only positively stated purpose or utility for the silica is to reduce tackiness and improve the free flowing characteristics of the developer 55 powder.

In British Patent Specification No. 1,172,839 it is taught that the inclusion of a minor proportion of hydrophobic metal salt of a fatty acid in an electrostatic developer overcomes certain problems as-

sociated with the use of prior art toner and carrier materials. Among the problems are the tendency of the toner to form unwanted deposits which interfere with copy quality and the long term abrasive affects of carriers and some toners. The metal salt of a fatty acid overcomes these problems, however, it has been observed that excessive buildup of the metal salt can likewise cause degradation of copy quality.

70 In U.S. Patent 3,552,850 issued to Stephen F. Royka et al, it is taught to employ a dry lubricant when employing a blade cleaner in an electrostatographic imaging system. This patent, however, does not teach how to control the deleterious buildup of dry lubricant.

75 In the following examples further define, describe and compare exemplary methods of preparing the development system components of the present invention and of utilizing them in a development and cleaning process. Parts and percentages are by weight unless otherwise indicated. The examples, other than the control examples, 80 are also intended to illustrate the various preferred embodiments of the present invention.

#### EXAMPLE I

95 The vitreous selenium drum of an automatic copying machine is corona charged to a positive voltage of 800 volts and exposed to a light and shadow image to form an electrostatic latent image. The 100 selenium drum is then rotated through a magnetic brush development station. A control developer comprising 2 parts of toner, containing a polystyrene resin and 100 parts of steel shot carrier beads. The 105 toner particles have an average particle size of 12 microns and the carrier beads an average particle size of 125 microns. After the electrostatic latent image is developed in the developing station, the resulting 110 toner image is transferred to a sheet of paper at a transfer station. The residual toner particles remaining on the selenium drum after passage through the transfer station is removed by three different techniques. In each case, and in subsequent examples, it is to be understood that a clean 115 selenium drum is employed in the examples.

One technique employs a cylindrical 120 brush having an overall diameter of 4 inches, a 15 denier polypropylene having a pile height of 3/8 inch, and a fiber density of 54,000 fibers per square inch. The brush is positioned against the drum to permit a 125 fiber interference of 0.1 inch and is rotated at 175 revolutions per minute. Initial copy quality is excellent, however, after 25,000 copies, background density is very high, resolution is markedly decreased, image fill 130

in solid and line copy is poor and edge definition is poor. Inspection of the drum reveals slight signs of wear and a significant buildup of toner on the surface 5 thereof.

- A second technique employs a cleaning web of the type disclosed by W. P. Graff, Jr. et al in U.S. Patent 3,186,838. A non-woven rayon web contact pressure of 18 10 pounds per square inch, web-photoreceptor relative speed of 1.5 inches per second, and a web contact arc distance of 1/8 inch are employed. After the copying process is repeated 5000 times, the copies show fairly 15 good line contrast and little background deposit. However, large solid areas possess a washed out appearance. Micrograph studies of the drum surface reveal a significant buildup of toner film.
- 20 A third technique employs a doctor blade cleaning mode of removing residual toner. A rectangular 1/16 inch thick strip of elastomeric polyurethane material, having one end chamfered to form a cleaning 25 edge having an angle of 60°, is positioned parallel to the axis of the drum. The chamfered edge of the blade is held at a chiseling rather than wiping attitude with respect to the moving drum. The vertical 30 resultant force employed to press the entire blade edge against the drum surface is about three pounds as read on a spring scale. Initial copies reveal good copy quality in all respects, however, after 2000 35 copies, image quality is markedly inferior showing high background density, poor image fill and decreased resolution. Inspection of the drum reveals a significant buildup of toner on the imaging surface.
- 40 The foregoing illustrates the problem encountered when employing a typical toner material which of its very nature has a tendency to build up on the photoreceptor. The increasing buildup is undoubtedly the 45 main cause of decline in copy quality.

#### EXAMPLE II

The developer procedure of Example I is repeated except that the developer is modified in the following manner: 0.1 part of 50 zinc stearate having a particle size distribution of 0.75 to 40.0 microns is gently folded into one part of toner. The resulting mixture is thoroughly milled in a Szegvari attritor for 10 minutes. After developed 55 image transfer, as in Example I, the doctor blade and technique of Example I is employed except the blade force used is 0.2 pounds. After 2000 cycles, the copies are characterized by high density and high 60 background deposits. The surface of the selenium drum will be observed to have an excessive film buildup. The film deposit is either zinc stearate or a combination of the same with toner.

65 By increasing the blade force on the

photoreceptor drum to three pounds copy quality remained good through 2000 cycles.

The foregoing example illustrates that by employing a representative friction-reducing material, i.e., zinc stearate, in the developer 70 composition, coupled with a cleaning means supplying sufficient force during cleaning, deleterious film buildup is effectively controlled.

The following examples illustrate that by 75 employing a comparatively abrasive material in conjunction with the film forming lubricant, copies of exceptionally high quality are obtained by an even more effective control of film buildup. 80

#### EXAMPLE III

The developing procedure of Example I is repeated except that the developer is modified in the following manner: To the toner of Example I, 0.25% of zinc stearate 85 is added and milled in a Szegvari attritor for ten minutes. Thereafter, 1.0% by weight of a treated submicron silicon dioxide is added and milled for an additional ten minutes. The treated silicon dioxide 90 particles are produced by flame hydrolysis decomposition of pure silicon tetrachloride in the gaseous phase in an oxyhydrogen flame at about 1100°C followed by reaction in a heated fluidized bed reactor 95 with dimethyl dichlorosilane. 75% of the silanol groups present on the surface of the freshly prepared silicon dioxide particles are reacted with the silane in the fluidized bed reactor. The silicon dioxide particles 100 have 3 silanol groups per 100A<sup>3</sup> of a surface prior to reaction with silane. Analysis of the final product reveals 99.8% SiO<sub>2</sub> and the balance carbon, Cl, heavy metals, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Na<sub>2</sub>O. The particle size is between 10-30 millimicrons and the surface area is 90-150 m<sup>2</sup>/g. 105

The relative coefficient of friction values for the several materials, determined by the technique described above, are as follows. Selenium 5.23, toner 3.92 and zinc stearate 0.67. The toner has a Shore Durometer hardness of greater than 100 on the A and B scale, zinc stearate 66 on the A scale and 52 on the B scale. The treated 115 silicon dioxide has a hardness of 5 on Moh's scale. After developed image transfer as in Example I, the blade cleaning technique of Example I is employed utilizing a blade force of 3 pounds. After 120 2000 cycles, the copies are characterized by the same exceptionally high image quality as the initial copies. Inspection of the selenium drum will reveal a film buildup of less than 300Å. 125

#### EXAMPLE IV

The process of Example III is repeated except the dual additive consists of 0.25% zinc stearate and 1.0% untreated submicron silicon dioxide. The silicon dioxide 130

- is identical to that of Example III except it is not treated to render it organophilic. The process is operated at a relative humidity of 80% at an average temperature of 75°F. The background density, resolution, image fill in line copies and edge definition are good in initial copies. However, after 900 copies, background density has more than doubled, resolution has decreased, image-fill in line copies is poor and edge-definition is poor. The photoreceptor reveals a dull damp claylike film which cannot be removed by ordinary cleaning techniques.
- 15 The same process carried out at a relative humidity of 30% at 75°F yields excellent copies after 2000 cycles. No claylike film is observed on the photoreceptor surface.
- 20 When the treated silicon dioxide of Example III is employed in the composition under the high relative humidity condition of 80% at 75°F image quality remains excellent and no colloidal silica deposit is observed on the photoreceptor.
- 25 It is believed that the voluminous, high surface area, untreated silica acts as desiccant and the water taken up by the additive deleteriously affects all aspects of the development and cleaning steps of the process. Under comparatively dry conditions this is not observed.

#### EXAMPLE V

The developing procedure of Example III is repeated except instead of zinc stearate, 0.25% of copper stearate is employed. After 2000 cycles, this developer yields copies of good quality in every respect. The film buildup on the photoreceptor

40 does not exceed 300Å.

Although specific materials and conditions are set forth in the foregoing examples, these are merely intended as illustrations of the present invention. Various other suitable toner components, additives, colorants, carriers and development techniques such as those listed above may be substituted for those in the examples with similar results. Other materials may also

50 be added to the toner or carrier to sensitize, synergize or otherwise improve the imaging properties or other desirable properties of the system.

Reference is made to our copending 55 British patent application 46890/72 (Serial No. 1 402 009).

#### WHAT WE CLAIM IS:—

1. An electrostatographic developing material comprising particles, said particles 60 including (1) divided electroscopic toner material; (2) 0.01 to 10.0 percent by weight based on the weight of said toner material of a metal salt of a fatty acid; and (3) 0.01 to 10.0 per cent by weight based on the 65 weight of said toner material of submicron

size colloidal particles that are silicon dioxide particles having surface silicon atoms chemically attached through silicon-oxygen-silicon bonding to silicon atoms having 1 to 3 organic groups directly attached thereto by silicon-carbon bonding.

5 2. The developing material of Claim 1 wherein said metal salt is zinc stearate.

3. The developing material of Claim 1 or 2 wherein said metal salt is present in 75 from 0.1 percent to 2.0 percent by weight based on the weight of said toner; and said modified silicon dioxide particles are present in from 0.1 percent to 2.0 percent by weight based on the weight of said toner 80 material.

4. The developing material of any one of claims 1 to 3 wherein said modified silicon dioxide particles have an average particle size of 1 to 500 millimicrons. 85

5. The developing material of Claim 4 wherein said average particle size is 10 to 100 millimicrons.

6. The developing material of Claim 4 wherein said average particle size is less 90 than 30 microns.

7. The developer material of any of Claims 1 to 6 including from 10-1000 parts by weight of carrier particles per part of toner material, said carrier particles being 95 larger than said divided toner material.

8. The developing material of claim 1, substantially as described with reference to the Examples.

9. A process of developing an electrostatic latent image comprised by a surface, said process comprising

developing an electrostatic latent image by the developing material of any one of Claims 1 to 8, to give a developed image 105 corresponding to said latent image.

10. The process of Claim 9, comprising removing at least a portion of at least any residual developed image from said surface by a force which causes the toner, metal 110 salt and said modified silicon dioxide particles of said developing material to be wiped across at least a portion of said surface.

11. The process of Claim 10 wherein the combination of said force and the 115 abrasive character of said modified silicon dioxide particles is sufficient to maintain the buildup of said metal salt on said imaging surface in the submicron range without completely removing said buildup. 120

12. The imaging process of Claim 10 or 11 wherein said force is applied via a cleaning blade.

13. The imaging process of Claim 10 or 11 wherein said force is applied via a 125 cleaning web.

14. The imaging process of Claim 10 or 11 wherein said force is applied via a cleaning brush.

15. The process of any one of Claims 130

10 to 14, comprising repeating the process sequence at least one time.

16. The process of Claim 9, substantially as described with reference to the 5 Examples.

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Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd, Berwick-upon-Tweed, 1975.  
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.